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DIELECTRIC AND OPTICAL PROPERTIES OF GAMMA-IRRADIATED COMPOSITES BASED ON NITRILE BUTADIENE RUBBER AND ZIRCONIUM OXIDE NANOPARTICLES

R. F. Khankishiyeva

Institute of Radiation Problems of ANAS
renanamazova0@gmail.com

Abstract: This paper presents an experimental analysis of the dose effect during gamma irradiation of butadiene nitrile rubber nanocomposite samples. ZrO_2 filled polymer were irradiated in the dose range of 100, 150, and 250 kGy in a Co^{60} irradiation source. The dielectric and optical properties of the irradiated materials were studied. The experimental results show an improvement in both of these parameters as dose increases, indicating the predominance of cross-linking over oxidative degradation. Also, was studied the morphology of nitrile rubber composites by SEM.

Key words: nitrile-butadiene rubber (NBR), polymer nanocomposites, radiation crosslinking, dielectric properties, optical properties

1. Introduction

In recent years, regardless of the type of base polymer (thermoplastic or thermoset), great attention has been paid to composite materials used in wide areas such as microelectronics, optics, and also for ordinary engineering purposes [1]. It is known that most polymeric materials are inherently electrical insulators [2]. However, they can be made electrically conductive in various ways, for example, by creating conjugated double bonds in the main polymer chain [3], introducing a donor–acceptor complex into the polymer matrix [4] and adding conductive fillers, such as metal powders or carbon black [5-8].

It is well known that the electrical conductivity in polymers can be significantly improved by irradiation [9]. The increase in the conductivity of irradiated polymers can be explained by the formation of conjugated structures. Also, irregularities in the polymer chain can cause an abrupt mechanism that improves conductivity [10].

Currently, nanoparticles are most in-demand as fillers for polymeric materials. Since, when compared with traditional polymer microcomposites, nanocomposites show significant improvements in physical properties, such as thermal conductivity and dielectric properties (resistivity, dielectric constant, dielectric strength, tensile properties, heat resistance, fire resistance, etc. [11 -13]. These observations are mainly associated with exceptional properties.

It is known that composite systems containing fillers such as TiO_2 [14], $BaTiO_3$ [15] and Al_2O_3 [16] are used to increase the dielectric constant of silicone elastomers.

We studied materials which are consisted of a thermoplastic elastomer containing Fe and NiFe powders with a volume fraction of 0.1 to 0.5 [17]. With the addition of ferromagnetic nanopowders, the bulk and surface resistances of the composites decreased by more than seven orders of magnitude, and the dielectric constant increased by 10 times.

The selection of nano-ZrO_2 as a filler in the study was established on the properties of this oxide (high impact strength and mechanical strength, resistance to abrasion and corrosion) which can improve the mechanical, optical and electrical properties of the elastomer. Due to its hardness, optical transparency, and high refractive index [18], it has found a wide range of applications in the various fields. These materials are used as interferometric filters in photonics, as a coating for laser mirrors.

The present study is aimed to clarify the effects of γ-radiation on the electrical and optical properties of nitrile butadiene rubber (NBR) filled with ZrO_2 nanopowder.

2. Materials and measurements

The object of the study is high molecular weight nitrile butadiene rubber (NBR) of the SKN-40 brand (Russia), in which the acryl-nitrile (AN) content in the molecule was 40%.
NBR rubber macromolecules consist of static distributed units of butadiene and acrylonitrile.

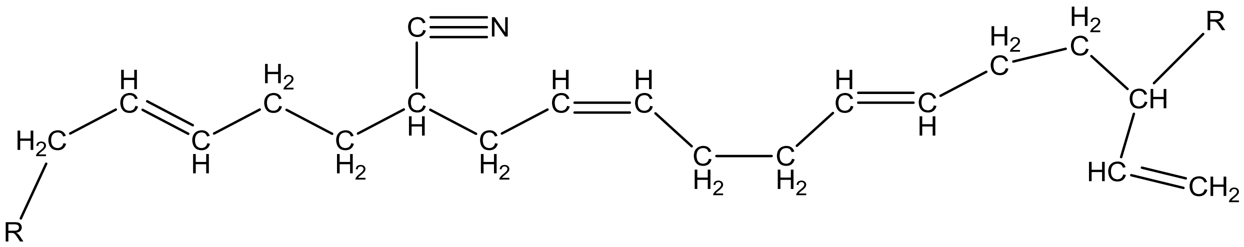

Fig. 1. Scheme of nitrile butadiene rubber

Zirconium dioxide (ZrO_2) nanopowder with a specific surface area of 160 m^2/g and a size of 30-35 nm from SkySpring Nanomaterials Inc, Houston, USA was used as activation of the crosslinking process.

In the process, benzene disulfochloride (DSCB) was used as a crosslinking agent, which readily interacts with NBR macromolecules [18].

NBR-based nanocomposites (Table 1.) were prepared on two rollers (outer diameter 470 mm, working distance 300 mm, roll rotation speed 24 rpm and friction coefficient (1: 1.4) by following ASTM D3182-07.

For the obtaining plates, the elastomeric mixture is vulcanized on a hydraulic press at a temperature of 423 K for 40 minutes. The irradiation of elastomeric mixtures was carried out by beams at a dose rate of 4.9 kGy/h at room temperature at a Co^{60} source with various doses (100, 150 and 250 kGy).

Table 1. Formulations for butadiene nitrile rubber nanocomposites

Ingredients	Irradiated doses		
	100 kGy	150 kGy	250 kGy
NBR	100	100	100
ZrO_2	6,0	6,0	6,0
DSCB	3,0	3,0	3,0
Naphthenic oil	5,0	5,0	5,0

The dielectric parameters (ε, tanδ) of the samples were measured using an E7-20 immittance meter (MNIPI, Belarus) in the frequency range from 25 Hz to 1 MHz. Depending on the irradiation dose thin films were prepared for each sample. Before measurements, a thin layer of foil was applied to the upper and lower surfaces of the films and then they have placed between two metal electrodes for measurement.

UV-visual studies of NBR / ZrO_2 / DSCB were studied by using Specord 210 Plus UV-Vis spectrophotometer in the wavelength range of 190–1.100 nm.

By a Scanning Electron Microscope (SEM) from the company CARL ZEISS SMT AG, (Germany), the topography of the surface, structure, and phase composition of the composite material was studied.

3. Results and discussion

3.1 Dielectric properties

In this research, the dielectric properties of nanocomposites based on NBR, radiation vulcanizates were investigated. The addition of nano ZrO_2 into the polymer mixture together with other low molecular weight compounds (DSCB), leads to a significant change in the dielectric loss.

It is well known that polarization of samples is observed when an electric field is applied to rubber. Generally, the polarization of a dielectric in the presence of an electric field includes two factors: relaxation polarization and resonant polarization. The first plays a major role at low frequencies and depends on the structure of the understudy composite. The latter plays an important role at high frequencies. As a result of polarization, uncompensated (space) charges appear on the surface of the dielectric, as well as in its volume. [19]

Differences in microstructure, pores, defects, etc., are the main sources of relaxation polarization, but they do not play a role at higher frequencies [20]. This is effect often called the Maxwell-Wagner (MW)effect. In addition, interfacial polarization (caused by the difference in the electrical properties of the rubber ingredients) can be observed under the influence of an electric field.

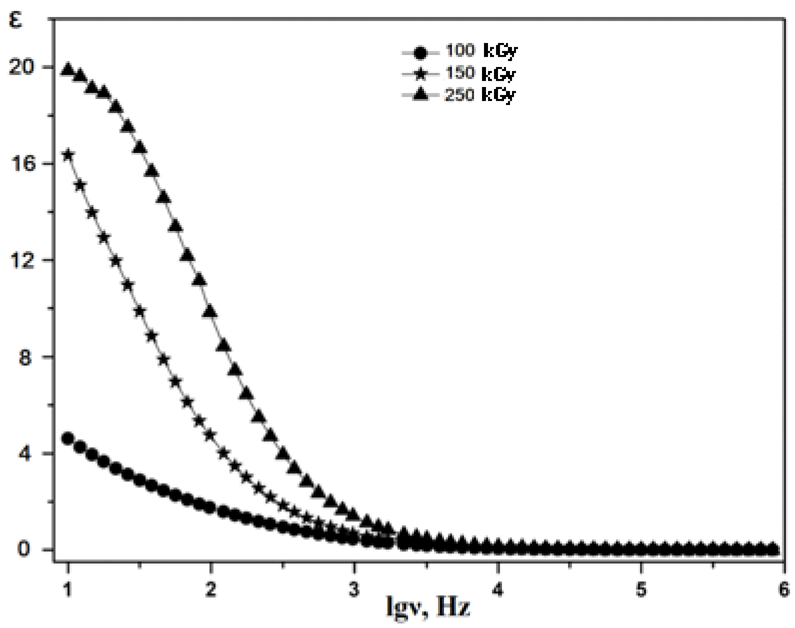

Fig. 2. Frequency dependence of the dielectric constant of irradiated nanocomposites (NBR + DSCB + ZrO_2)

According to the obtained experimental results, interfacial polarization leads to high dielectric constant and losses, which rapidly decrease with increasing frequency of the electric field. The frequency dependence of the dielectric constant (ε) of NBR-based composites at different radiation doses is shown in Fig. 2. Dielectric measurements show that for samples irradiated at 100 kGy doses, the dielectric constant is lower than for samples which are irradiated with 250 kGy at low frequencies.

This suggests that at low frequencies, electronic, ionic, dipole and space charges (surface charge) contribute to the dielectric constant. However, in the frequency range of MHz, the contribution of the polarization of the space charge is minimized and the dielectric constant decreases. [21]

The dependence of dielectric loss on frequency changes is shown in Fig. 3. tgσ= f (lgν), which leads to a drag dielectric loss at low frequencies and leads to a decline at high frequencies.

An increase in the dielectric constant and the dielectric loss after exposure to a dose of γ radiation of 250 kGy, may be due to atomic displacements nanoparticles of the composite. Atomic displacements create various types of lattice defects. Defects affect macroscopic physical properties. In this case, the off-center shift of ZrO_2 ions from normal centers also leads to a distortion of the structure. This can lead to an increase in polarization and consequently, to an increase in dielectric constant and loss tangent. [22]

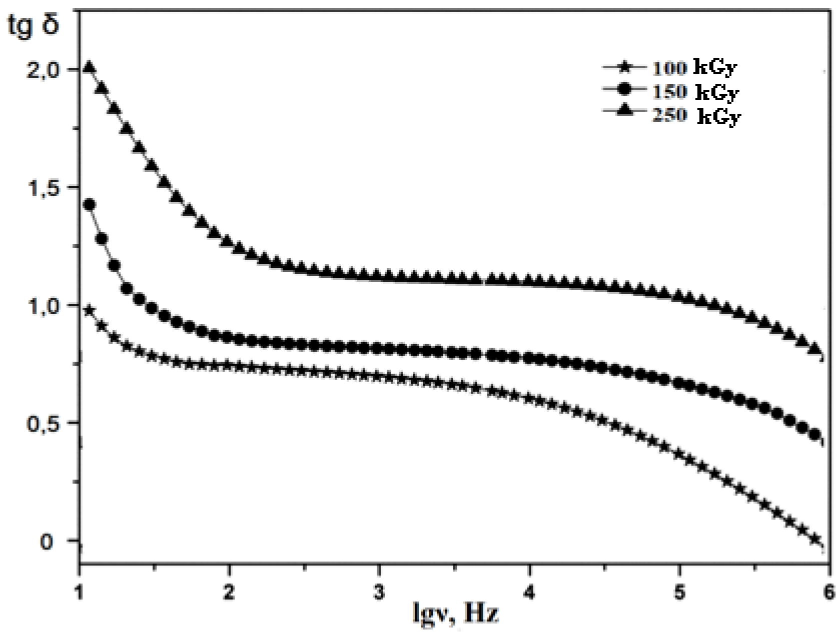

Fig. 3. Frequency dependence of the dielectric loss tangent of irradiated nanocomposites (NBR + DSCB + ZrO2)

As well as an increase in the dielectric constant in the low-frequency region with an increase in the radiation dose is explained by interfacial interaction between the polymer and the surface of the nanoparticles.

3.2 UV-Vis Analysis

It is the knowledge that [23], the electrical conductivity of rubbers is related to the concentration of double bonds, the presence of which can be determined by UV-VIS spectroscopy. Figure 4. represents the UV-Vis spectra of a composite modified with nano ZrO_2 at room temperature after irradiation with various doses. As illustrated in the figure, depending on the radiation dose, some of the observed signals in the UV-Vis spectrum remained unchanged and some of them showing the small shift in the absorption peak towards longer wavelength changed, also, new signals appeared.

It turned out that, the higher the irradiation dose, the more ultraviolet rays can be absorbed by NBR-based hybrid nanocomposite films. Compared to a pure NBR film, the transparency of the NBR/ZrO_2/DSCB films of the composite has been increased. On the other hand, for nanocomposites we can say that the peak of the spectrum was shifted from 317 nm to 396 nm, depending on the dose. As a rule, the signals observed in NBR/ZrO_2/DSCB samples show $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electronic transitions [24].

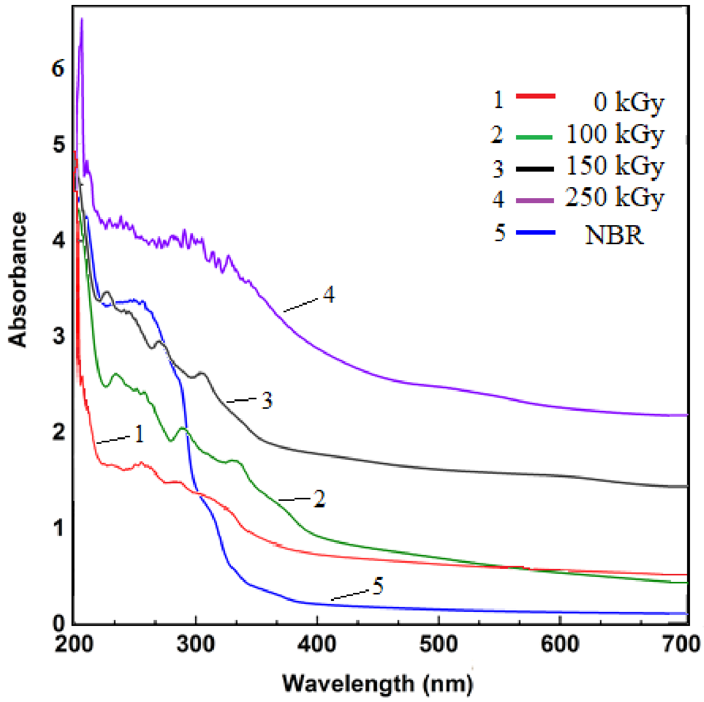

Fig. 4. UV-Vis spectrum of NBR and NBR / ZrO_2 / DSCB nanocomposite obtained by gamma radiation

3.3 SEM analysis

The topographic and chemical composition of the composite can be appreciated by the results of SEM analysis. Fig. 5. shows the surface morphology of the irradiated sample at a dose of 250 kGy. As can be seen from the figure, the surface of the irradiated film is not smooth and dispersed particles of ZrO_2 are spherical, as well as small surface cracks a slight agglomeration is observed.

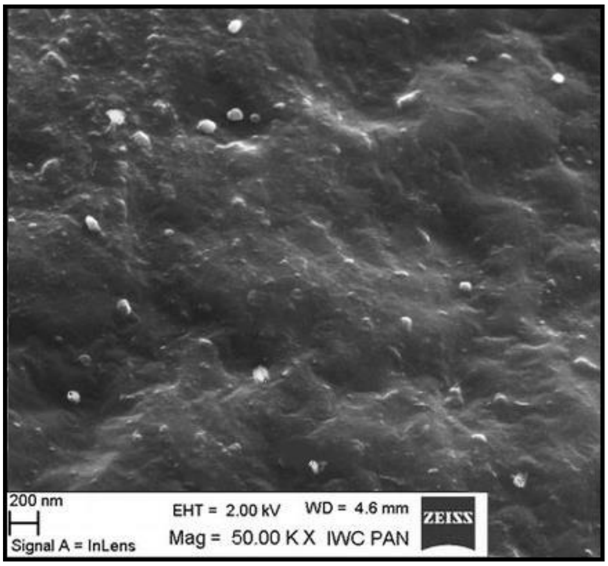

Fig. 5. SEM image of the surface of the NBR / ZrO_2 / DSCB nanocomposite lowed by gamma irradiation by a dose of 250 kGy.

4. Conclusion

As a result of the work, we studied polymer nanocomposites based on NBR obtained by modification and the radiation-chemical method. Changes in electrical and optical properties caused by gamma irradiation were considered. Maximum electrical conductivity was found for the sample irradiated with a dose of 250 kGy. The optical absorption spectra indicate the presence of ion beam induced conjugation. In sum, this new scientific knowledge will help to obtain new constructive and functional devices and gamma irradiation can be used as a tool for the development of elastomeric electrolytes by increased ionic conductivity.

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ДИЭЛЕКТРИЧЕСКИЕ И ОПТИЧЕСКИЕ СВОЙСТВА ГАММА-ОБЛУЧЕННЫХ КОМПОЗИТОВ НА ОСНОВЕ БУТАДИЕН-НИТРИЛЬНОГО КАЧУКА И НАНОЧАСТИЦ ОКСИДА ЦИРКОНИЯ

Р. Ф. Ханкишиева

Резюме: Представлены результаты анализа научного исследования, посвященного изучению влияния дозы гамма-облучение нанокомпозитных образцов на основе бутадиен-нитрильного каучука. Полимер, наполненный ZrO_2, облучали в диапазоне доз 100, 150 и 250 кГр в источнике Co^{60}. Изучено диэлектрические и оптические свойства облученных материалов. Полученные экспериментальные результаты показывают улучшение этих параметров при увеличении дозы радиации, что указывает на преобладание процесса сшивания над деструкцией и образованием С-С новых связей. Также, с использованием метода сканирующей электронной микроскопии (СЭМ) была изучена морфология исследуемого нанокомпозита

Ключевые слова: бутадиен нитрильный каучук, полимерные нанокомпозиты, радиационная сшивание, диэлектрические свойства, оптические свойства.

BUTADİEN-NİTRİL KAUÇUKU VƏ SİRKONİUM OKSİD ƏSASLI QAMMA ŞÜALANMIŞ KOMPOZİTLƏRİN DİELEKTRİK VƏ OPTİKİ XASSƏLƏRİ

R. F. Xankişiyeva

Xüalasə: Aparılan elmi tədqiqat işində, butadien nitril kauçuku əsasında alınmış nanokompozit nümunələrə, qamma şüalanmanın təsirinin öyrənilmişdir. Doldurucu kimi ZrO_2 istifadə olunan polimer qarışığı Co^{60} mənbəyində 100, 150 və 250 kQr dozalarda şüalandırılmışdır. Şüalanmış nanokompozitlərin dielektrik və optiki xassələri tədqiq edilmişdir. Alınmış təcrübi nəticələrə əsasən müəyyən olunmuşdur ki, radiasiya dozasının artması ilə hər iki parametrdə yaxşılaşma müşahidə olunur, bu da tikilmə prosesinin, destruksiya prosesindən daha sürətlə getməsi və yeni C-C rabitələrinin yaranması ilə izah oluna bilər. Bundan başqa, skanedici elektron mikroskop (SEM) metodundan istifadə etməklə, tədqiq olunan nanokompozitlərin morfologiyası öyrənilmişdir.

Açar sözlər: butadien nitril kauçuku, polimer nanokompozitlər, radiasion tikilmə, dielektrik xassələr, optiki xassələr.